Characterization of gold-, tin- and iron microenvironments in nanocomposites with the help of Mössbauer spectroscopy

Thesis

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1. Introduction

The modern technology has very strict requirements for the materials used, therefore it is necessary to develop new types of materials for the development. One of these newer type of materials are the nanomaterials whose can have exceptional properties compared to bulk phase materials and more importantly, these properties can be tuned for different applications. In our study, we have studied nanomaterials with exceptional biocompatibility and biodegrability. These materials can help in advanced medical applications, they can act as carriers for targeted drug delivery or they can be used in hyperthermia treatments. In addition, nanocomposites can be used in other areas, such as catalysis or waste treatment. However, the oxidation state, phases and phase transitions, crystal- and molecule structure, of the nanomaterials must be known for successful applications. During my Ph. D. work, I synthetized and characterized butyl-dithiol functionalized gold- and carboxylic acid functionalized iron-oxide nanoparticles, as well as nanoparticle precursors (hyperalcaline tin(II) hydroxides) and possible drug precursors (dioxime based compounds).

2. Objectives

My Ph. D. work had four objectives:

I. Stabilization with thiol is a routine practice in the synthesis of gold nanoparticles, however the exact qualitative and quantitative characterization of gold-sulfur bonds is not fully known. To understand better the gold-sulfur bond, we should synthetize gold nanoparticles with 2 nm diameter, where the shell/core ratio high enough to be possible to determine the valance state and microenvironments of gold in both phases. Our goal was to determine the valance states and microenvironments of the gold atoms in the above described nanocomposites, with ^{197}Au Mössbauer spectroscopy, also to determine the occurrence of these microenvironments and compare them with our model of these nanocomposites.

II. It is known that iron oxide based nanocomposites can play a major technological role, the industry aims to produce nanoparticles quickly, efficiently and cheaply. The precipitation method can be a good choice for manufacturers as they can quickly and sparingly produce spherical nanoparticles in large quantities. However, the precipitation method also has disadvantages too, the most significant disadvantages are the mixing of phases and the absence of stoichiometry and these two disadvantages can lead to serious difficulties in the quantitative and qualitative analysis of the iron oxide-based nanocomposites. Due to these difficulties, during the Mössbauer analyses of nanomagnetites, the determination of maghemite and magnetite phases is not always lead to satisfactory results if we use the

conventional model based fitting method. The reasons for this failure can be the particle size and nonstoichiometry induced superparamagnetic, change of Verwey temperature and changes in the shape of the spectral lines. We were looking for an answer whether it is possible to determinate the magnetite/maghemite ratio in the carboxylic acid functionalized nanomagnetites made by coprecipitation method, by the model independent hyperfine field distribution evaluation method of the Mössbauer spectra? Also, we wanted to determine, by ^{57}Fe Mössbauer spectroscopy with the help of other methods (RAMAN, XRD, FTIR, TEM, PAS) whether the short chained carboxylic acids (glycolic-, propionic-, tartaric-, caproic-, lactic-, caprylic-, malic-, mandelic- and salicylic acid) can or cannot change directly the magnetite/maghemite ratio in carboxylic acid functionalized nanomagnetites made by coprecipitation method? We also wanted to answer the question, posed by the novel point of view, whether functionalization with individual carboxylic acids can directly oxidize or reduce iron oxide nanoparticles? If the answer is yes then, which feature of carboxylic acids can be associated with this effect?

III. Metal bis-glyoxime based compounds may be useful as anticancer drugs, and for such treatments, greater selectivity can be achieved if we transfer the drugs to the targeted cells by the use of nanocarriers. In the last decades in our laboratories dozens of new iron-bis-glyoximes were synthetized and characterized in international collaboration. ^{57}Fe Mössbauer spectroscopy was the main tool to determine the valance and spin state of the iron. In previous studies, it was determined that in iron-bis-glyoximes with small side chains the central iron is always in Fe^{II} low spin state. Our aim in this work was to characterize the newly synthesized, novel iron-bis-glyoxime complexes to determine the oxidation and spin state of iron atoms by ^{57}Fe Mössbauer spectroscopy.

IV. Due to the development of technology, it has become important to study the behavior of materials in extreme conditions. Such extreme condition can be the extreme high or low temperature, pressure or even pH too. Recently our research team has successfully defined the structure of the hyperalcaline (pH> 13) tin(II) hydroxide [1]. To obtain additional information on the chemical bonding of the hyperalcaline tin(II) hydroxide, our goal was to understand better the ^{119}Sn Mössbauer spectra of this material, especially the reason of the asymmetric line intensity representing our samples. Therefore, ^{119}Sn Mössbauer spectra were measured as a function of temperature to determine, that the asymmetric Mössbauer spectrum is a result of the texture effect or the superposition of multiple microenvironments or it is the result of the Goldanskii-Karyagin effect?

3. Summary of the new scientific results

In my dissertation, I presented the characterization of nanocomposites which may have medical applications in the future. During my Ph. D. work, I synthetized many nanocomposites and characterized them mainly by Mössbauer spectroscopy. The results of these studies were published in 9 referenced articles and 11 presentations. My theses can be found at the end of the following subchapters.

3.1. Observation of new gold microenvironments in butyl dithiol functionalized, gold nanocomposites with average 2.2 nm diameter

We synthetized butyl dithiol functionalized gold nanoparticles with modified Brust-Schiffrin method [2]. The samples were characterized by ^{197}Au Mössbauer spectroscopy, high-resolution electron microscopy, thermogravimetry, X-ray diffractometry, UV-Vis- with Raman spectrometry. Mössbauer spectra was evaluated with MOSSWINN 4 program [3].

The particle size was determined from the electron microscopy measurement, it was found that the average diameter is 2.2 nm. Gold microenvironments and their quantity in the sample were determined by ^{197}Au Mössbauer spectroscopy. The defined gold microenvironments are in good accordance with the microenvironments in the literature of gold clusters [4]. I also determined the occurrence of the gold microenvironments from my model which model was based on geometry and chemical considerations, which supports the Mössbauer results.

Table 1 Mössbauer parameters and occurrence of microenvironments in butyl dithiol functionalized gold nanoparticles, determined from a 4.2 K ^{197}Au Mössbauer spectrum

component	δ / mm s^{-1}	Δ / mm s^{-1}	Γ / mm s^{-1}	*relative line intensity* / %
S	-1.10 (0.05)	-	2.11 (0.12)	46 (1)
D1	-1.06 (0.07)	2.02 (0.03)	2.06 (0.20)	34 (1)
D2	-0.08(0.10)	3.18 (0.39)	2.63 (0.53)	14 (2)
D3	0.55 (f)	7.70 (0.67)	3.20 (0.90)	5 (2)

Based on ^{197}Au Mössbauer result, supported by other methods and calculations my first thesis is the following: I have distinguished four different microenvironments in gold nanoparticles

functionalized with butyl dithiol by the help of ^{197}Au Mössbauer spectroscopy. These four microenvironments in our 2.2 nm particle sized nanocomposites are metallic gold (0) in the core and on the surface, and valance state +1 gold atoms bound to one or two sulfur atoms. The valance states of the gold atoms are determined by the analysis of the measured isomer shift and quadrupole splitting values. I also made a model for the structure of the butyl dithiol-functionalized gold nanocomposites, based on geometry and stereochemistry. The relative occurrences of all microenvironments obtained from this model match well those relative occurrences acquired from the Mössbauer results [5].

3.2. Functionalizing agent dependence of the oxidation state of nanomagnetites

Nanomagnetites were synthetized by modified Khalafalla coprecipitation method .with different carboxylic acids (glycolic-, propionic-, lactic-, malic-, mandelic-, tartaric-, caproic-, caprylic-, salicylic- and citric acid). The most accepted model for the structure of these nanocomposites is a magnetite core, which is covered by a maghemite shell which is covered by an organic layer.

The magnetite/maghemite ratio was determined mainly by hyperfine field distribution method of ^{57}Fe Mössbauer spectroscopy [6] (Hesse-Rübartsch method [7]) and by Raman spectroscopy [8]. The comparison of the phase ratios obtained by Mössbauer- and Raman spectroscopies can be seen on Fig. 1. Our results shown that the carboxylic acids used for functionalization can also change the magnetite/maghemit ratio of nanomagnetites beyond the preparation parameters known so far (pH [9] and particle size [10]). These results are supported by magnetic- and photoacoustic measurements too. The possible reasons for this phenome include the difference of the acidity of carboxylic acids, which is supported by our later results [11].

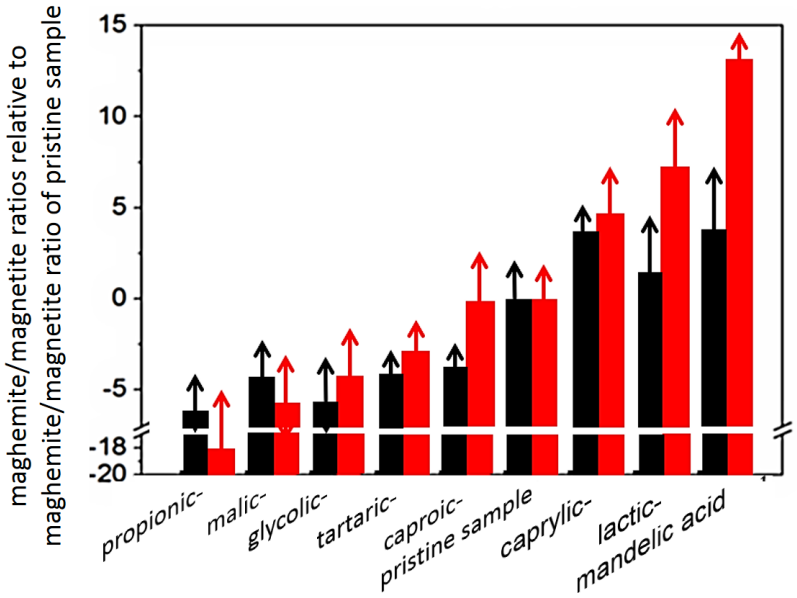

Figure 1 *Comparison of Mössbauer- (red) and Raman results (black) for the magnetite/maghemite ratio of carboxylic acid functionalized nanomagnetites*

The results shown in 3.2. can be summarized as: II. thesis: I have demonstrated by ^{57}Fe Mössbauer spectroscopy with the support of other methods (Raman-, Fourier transformed infrared- and photoacoustic spectroscopy, X-ray diffractometry and magnetization measurements), that the carboxylic acids with short carbon chains can influence the magnetite/maghemite ratio of coprecipitated iron oxide nanoparticles functionalized with carboxylic acids. I have found that the functionalization of nanomagnetites with carboxylic acids like mandelic-, caproic- and lactic acids, promotes the oxidation of iron oxide nanoparticles, meanwhile, the functionalization with other carboxylic acids, like tartaric-, propionic-, glycolic-, malic- and caprylic acid, promotes the reduction of the iron oxide nanoparticles even if the average particle size are nearly same in all of these nanocomposites [6, 11, 12, 13].

3.3. Effect of the ligands on the spin state of iron in iron-bis-glyoxime coordination compounds

Possible anti-cancer drug precursors (glyoxime based compounds) were synthetized by nitration of ketones. The valance and spin state of the iron were determined by ^{57}Fe Mössbauer spectroscopy. For the presentation of the results I will use the newly synthetized [iron(methyl-isopropyl)$_2$(2-imidazolidone)$_2$] complex and the [iron(methyl-ethyl-glyoxime)$_2$(2-imidazolidone)$_2$] complex from a previous study [14].

Room temperature ^{57}Fe Mössbauer spectra of [iron(methyl-ethyl-glyoxime)$_2$(2-imidazolidone)$_2$] and [iron(methyl-isopropyl-glyoxime)$_2$(2-imidazolidone)$_2$] can be seen on Fig. 2. The Mössbauer spectra clearly shown that iron is in Fe^{II} low spin state in the [iron(methyl-ethyl-glyoxime)$_2$(2-imidazolidone)$_2$] complex, opposed to the high spin Fe^{II} state which can be found in the [iron(methyl-isopropyl-glyoxime)$_2$(2-imidazolidone)$_2$] compound. A single doublet can be seen on both Mössbauer spectra (Fig. 3) whose Mössbauer parameters are characteristic to low spin (δ = 0.01 mm·s^{-1}, Δ = 1.71 mm·s^{-1}), and high spin (δ = 1.24 mm·s^{-1}, Δ = 2.68 mm·s^{-1}) Fe^{II} states [15].

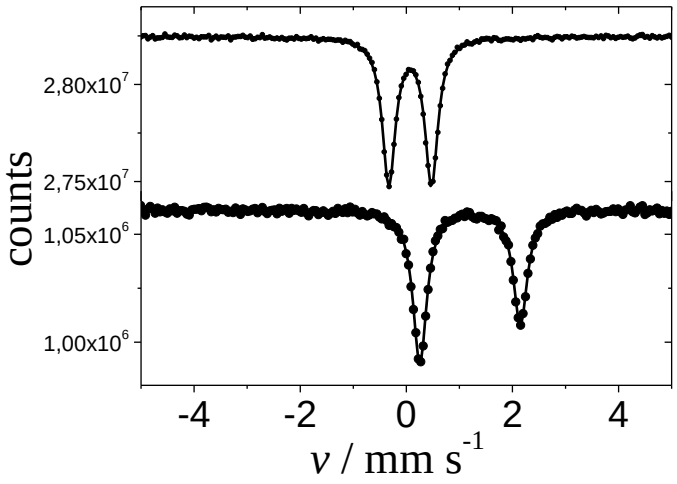

Figure 2 *300 K Mössbauer spectra of [iron(methyl-ethyl-glyoxime)$_2$(2-imidazolidone)$_2$] (top) and [iron(methyl-isopropyl-glyoxime)$_2$(2-imidazolidone)$_2$] (bottom) coordination compounds*

This difference is exceptional because the structure of the two compound is similar, and the first and second neighbor atoms of the irons are the same in both compounds. The central iron atom coordinated by 6-6 nitrogen atoms in bipyramid geometry in both complex, however the side chains of the glyoximes are different.(Fig. 3).

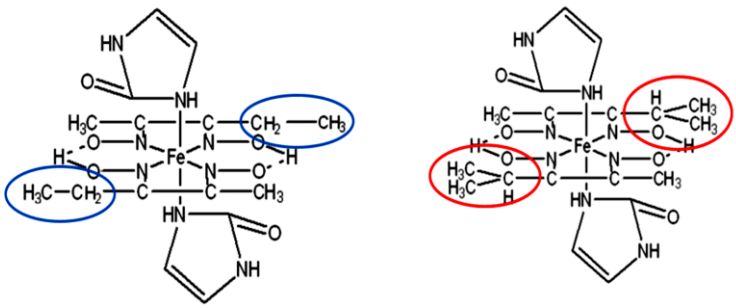

Figure 3 *Schemes for the structure of [iron(methyl-ethyl-glyoxime)$_2$(2-imidazolidone)$_2$] (left) and [iron(methyl-isopropyl-glyoxime)$_2$(2-imidazolidone)$_2$] (right) compounds*

It was already known [16, 17], that is in high spin Fe^{II} state in iron-bis-glyoximes, if they have (semi)planar structure if they not have axial ligands. However, in the case of iron(methyl-ethyl-glyoximes), if axial ligands are connected to the plane the favored spin state of the iron will be low spin. According to Németh et al. [14] the reason for the low spin state is the shortening Fe-N bond length which is caused by axial ligands. Our observations expand these results as in [iron(methyl-isopropyl-glyoxime)$_2$(2-imidazolidone)$_2$] type complexes the favored state of the iron is Fe^{II} high spin. The reason for this phenome is that the larger side chains of the glyoximes change the molecule geometry, which cause longer Fe-N (planar) bond length. This increase in bond length is so large that the new bond length will be longer than the critical 2.05 Å [18], therefore the high spin state will be favored. This observation is supported by DFT calculations too, which shown us that the Fe-N_{glyox} bond length in this type of complexes is 2.38 Å [19]. Therefore, our observations (Mössbauer and other methods) and the calculation are mutually supporting each other. Our results are a good addition to the previous results about the structure of iron-bis-glyoximes, the addition of axially ligands leads to Fe^{II} low spin state in the case of semi(planar) iron-bis-glyoximes, with the new effect that large spaced ligands linked to glyoximes causing the Fe^{II} high spin state to be favored again. With this information the spin state of the iron can be tuned in iron-bis-glyoxime based complexes [20].

Based on these, my III. thesis is the following: I have shown that the replacement of short carbon chain with small volume demand onto longer branching carbon chain with high volume demand in iron-bis-glyoxime-based complexes results in change of the spin state of iron atom from low spin state to high spin state. I observed this phenomenon with ^{57}Fe Mössbauer spectroscopy, the determination of the iron spin-states was done from the measured isomer shift and quadrupole splitting values. The reason for this phenomenon is that the molecule geometry changes, due to the increase of Fe–N bond length as an effect of the substitution of high-volume demand branching chains, results change of the favored spin-state of the iron atom [1, 3].

3.4. Observation of Goldanskii-Karyagin effect in frozen hyperalcaline tin(II)-hydroxide solutions

Hyperalcaline (pH > 13) tin(II)-hydroxide solutions were synthetized from tin(II)-chlorate and sodium-hydroxide, which solution can produce nanoparticles via self-assembly. The structure of these nanoparticles is depending on the structure on the tin(II)-hydroxide in the solution, the later was described in another Ph. D. work [21]. In my Ph. D. work, I have focused on an unexpected observation which were made during the ^{119}Sn Mössbauer measurements. Mössbauer spectra of frozen hyperalcaline tin(II)-hydroxide solutions measured at various temperatures (20-180 K) can be seen on Fig. 4. Each

Mössbauer spectrum consists only a single doublet, which Mössbauer parameters characteristic to tin(II) components [22]. It is worth to note, that subspectrum belonging to tin(IV) (impurity) nowhere can be seen, which proves that we managed to avoid the, otherwise very probable, oxidation of the sample.

Fig. 6 shows us that the line intensity asymmetry has temperature dependence. The asymmetry can be described if we fit each spectrum with 2-2 Lorentz curves and we compare these lines. The temperature dependence of the comparison of these lines shown on Fig. 5.

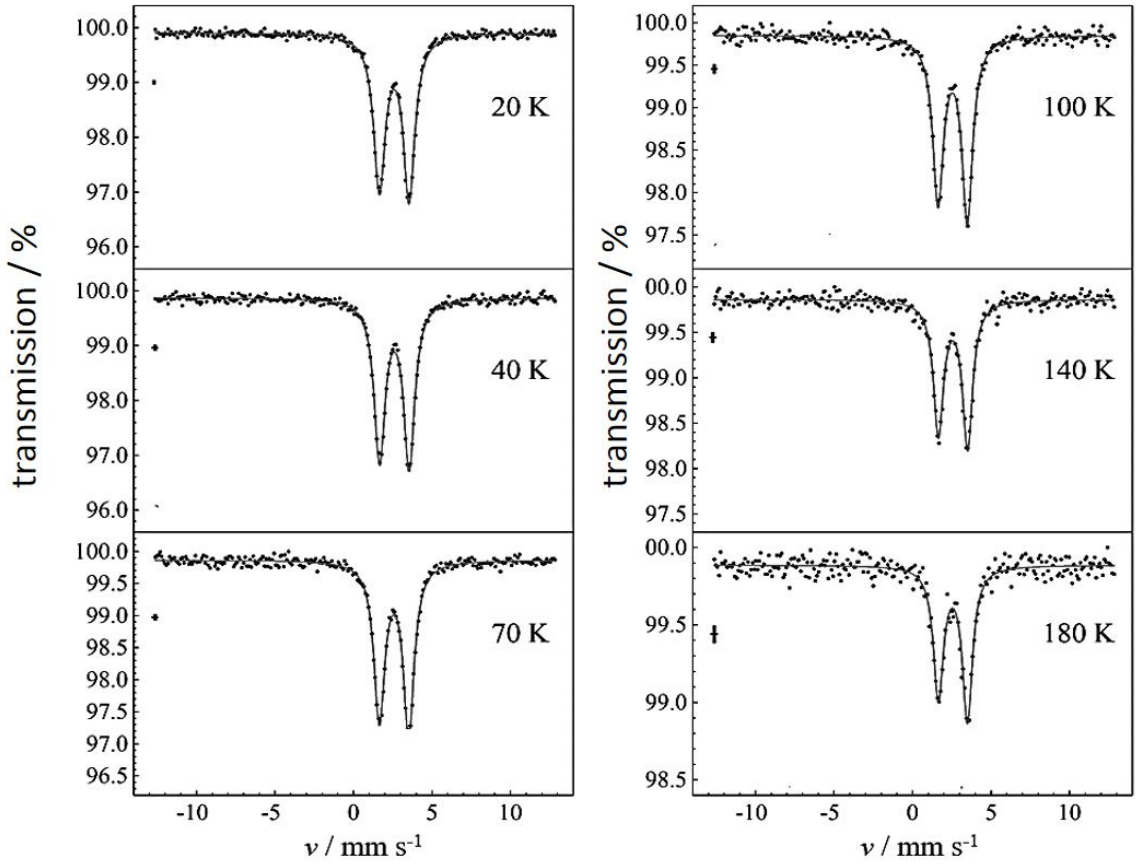

Figure 4 *^{119}Sn Mössbauer spectra of frozen hyperalcaline tin(II)-hydroxide solutions*

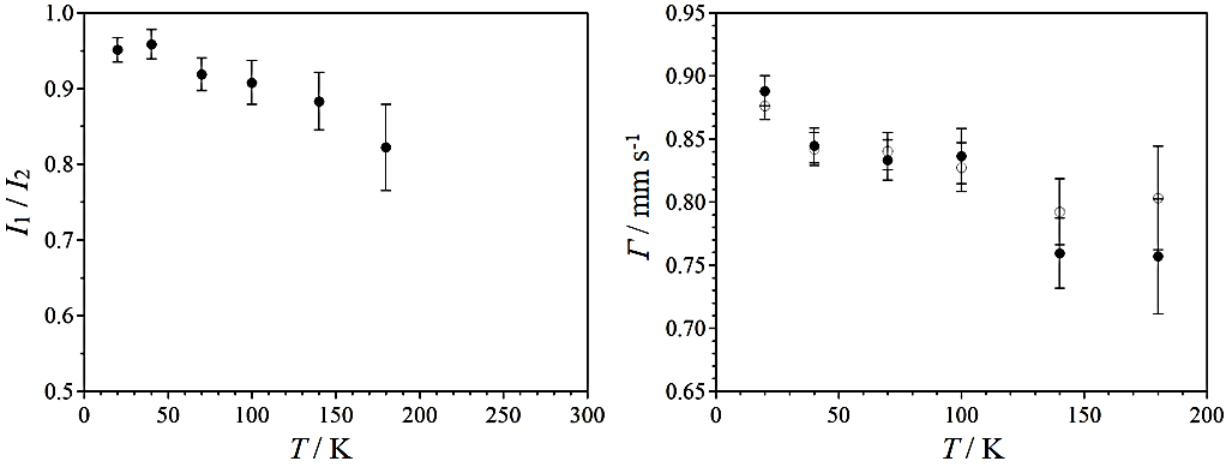

Figure 5 *Temperature dependence of the relative line intensity (left) and FWHWA (right) of doublet lines representing the frozen hyperalcaline tin(II)-hydroxide solutions*

Fig. 5 shows that the I_1/I_2 ratio approaching to one with the decrease of temperature, which excludes a very probable reason for the asymmetric line intensity, the texture effect [23]. According to Fig. 5 another possible reason for the asymmetry also can be excluded, the superposition of multiple subspectra, because measured linewidths follows the regular temperature dependence (for example on 180 K temperature the 0.783 (0.003) mm·s^{-1} linewidth is very close to the thinnest technically obtainable linewidth). This type of temperature dependent line broadening caused by the temperature dependence of lattice vibrations, which changes the probability of the Mössbauer effect [23]. This effect cause that the effective sample thickness increases as the temperature decreases and this thickening cause the line broadening [23]. Therefore, the measured linewidths prove that the sample indeed consists only one phase, so this excludes that the asymmetry can be caused by spectral superposition [24]. Taking into consideration the above described results, the most probable reason for this asymmetry remains the not so common Goldanskii-Karyagin effect [25, 26].

The relative doublet line intensities can be fitted with Goldanskii-Karyagin effect (assuming that our sample is anisotropy powder), where $k^2\left(\langle r_{\parallel}^2\rangle - \langle r_{\perp}^2\rangle\right)$ (aka the vibration anisotropy) is a fitting parameter. The measured/calculated line intensities and other Mössbauer parameters are summarized in Table 2. In Table 2 we can see that the vibration anisotropy decreases as the temperature decreases, which proves that the asymmetric line intensity is indeed caused by the Goldanskii-Karyagin effect Similar asymmetry is observed for α-SnF_2 [27]. According to Grimm rule [28], this means that in hyperalcaline solution the hydroxide ions behaves similarly as the fluoride ions. Theoretically similar behavior is also assumed for oxygen-tin bond too [29]. To summarize these results, there is Goldanskii-

Karyagin effect in frozen hyperalcaline tin(II)-hydroxide solution, which is caused by the nonbonding electron pair of the tin [30].

Table 2 Mössbauer parameters of frozen hyperalcaline tin(II)-hydroxide solutions (with Goldanskii-Karyagin effect, in parentheses the 1σ of the digit)

parameter/T	20 K	40 K	70 K	100 K	140 K	180 K
A_n	0.0802(4)	0.0789(5)	0.0673(5)	0.0533(6)	0.0376(6)	0.0226(5)
δ / mm·s^{-1}	2.486(3)	2.496(3)	2.472(4)	2.446(5)	2.467(6)	2.461(10)
Δ / mm·s^{-1}	1.890(5)	1.888(6)	1.872(7)	1.862(9)	1.857(12)	1.848(19)
$k^2(\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle)$	-0.43(6)	-0.33(8)	-0.57(9)	-0.72(11)	-0.69(16)	-1.08(25)
Γ / mm·s^{-1}	0.882(7)	0.843(8)	0.837(9)	0.832(13)	0.778(17)	0.783(27)

My IV. thesis: I have shown Goldanskii-Karyagin effect, i.e. anisotropy of lattice vibrations, in frozen solution of hyperalcaline tin(II) hydroxides, by the help of ^{119}Sn Mössbauer spectroscopy, based on the analysis of the temperature dependent intensity of asymmetric quadrupole lines. The Goldanskii-Karyagin effect can be explained in this sample by the effect of tin's non-bonding electron pair on the atomic vibrations [2, 4].

The observations described in this dissertation can be useful starting base and warning for the later synthesis of nanocomposites and Mössbauer studies. This work can also be useful in developments and applications of these nanocomposites.

4. Publications and references

4.1. Publications which are the base of the dissertation

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4.3. Other publications

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